Study of the degradation of an organophosphorus pesticide using electrogenerated hydroxyl radicals or heat-activated persulfate

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A B S T R A C T

The use of pesticides and their release into the natural environment constitutes a direct threat for the environment and the living beings especially the human health. Consequently, the development of technics to detoxify the pesticide residues to reduce at least areas and contaminated matrix is needed. In the present work, a comparative study was performed on the chemical oxidation of an organophosphorus compound, the dimethoate (DIM), with sulfate radicals and hydroxyl radicals. Both oxidants are generated in situ, the sulfate radicals were produced by heat-activation of persulfate (PS) and hydroxyl radicals were generated by water electrooxidation using a boron doped diamond anode (BDD). For both cases, the target molecule has disappeared but the selective reaction of sulfate radicals with organics led to the production of intermediates which are less biodegradable than DIM since the ratio between the biological oxygen demand (BOD_5) and the chemical oxygen demand (COD) has been divided by 2 within the first hour of the process. Whereas the BOD_5/COD ratio during the electrochemical oxidation of DIM via hydroxyl radicals showed that it was possible to render the solution biodegradable without reaching a complete mineralization. However, it has been shown that the presence of chlorides in the solution must be avoided because of the formation of undesired organochlorides during the process.

1. Introduction

The direct or indirect discharges of the effluents of the agricultural practices causes significant degradation of the ecosystems. Particularly, the effluents of the agricultural practices (phytosanitary treatments, wash of the material and the rinsing of atomizers) move through the matrix of the ground and reach streams and even groundwater. It should be noted that the majority of pesticides used in the past contained organochlorine molecules; the use of these molecules has been prohibited because of their high toxicity. Nowadays, the organochlorine compounds are replaced by organophosphorus molecules (OPP) which are more selective and have a lower persistence [1 3]. Dimethoate (DIM) is one of the most widely used organophosphorus insecticides in agricultural activities including olive cultivation in the Mediterranean region [4,5]. DIM is an indirect acting OPP insecticide, it is converted in the body into the active metabolite, demithoxon [6], it is a real risk of adverse health effects following chronic cumulative exposure found in fruit, especially when fresh fruit are consumed by children [7]. In 2016, its use for fruits and vegetables was prohibited in France.

Important quantities of product are discharged when farmers rinse atomizers and tanks containing the pesticide after its use. The objective is not to treat the polluted water after discharging the pollutant in the natural environment but rather to treat upstream the unused product. The use of biological processes for the pesticide treatments leads to the generation of very often secondary wastes [8]. To overcome this problem, several processes have been developed, the AOPs (Advanced Oxidation Processes) are based on the generation of highly reactive radicals which have high standard redox potential such as ($^{\cdot}OH$) ($E^{\circ}(^{\cdot}OH/H_2O) = 2.80$ V), and attack most of the organic molecules resulting in a partial or total decomposition [9 12]. The well known attack mode of $^{\cdot}OH$ can be hydrogen atom abstraction, addition to unsaturated bond and electron transfer. Recently, Mousset et al evidenced, using electro Fenton process, a fourth attack mode of $^{\cdot}OH$ through ipso substitution of the halogen atom [13].

The performances of various AOPs for OPP degradation were compared by Ikehata and El Din [8]: ozonation and ozone based AOPs such as O_3/H_2O_2, O_3/UV and O_3/H_2O_2/UV, direct photolysis and various photochemical processes such as TiO_2/UV [14 17]. Meijers et al. [18] showed that DIM was readily degradable by ozonation under particular conditions but no further studies were reported on the kinetics, by

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products, and pathway of this organophosphate insecticide degradation. Solar photocatalysis using titanium dioxide has been tested for DIM removal by Arques et al. [14]. It has been shown that although a complete disappearance of the target molecule has been achieved, the detoxification of the solution was not reached whatever the operating conditions. Using the same process, Evgenidou et al. [15] showed that the complete detoxification was reached only in the presence of photo Fenton system with perchlorate addition. Theses authors have studied the reaction mechanism of dimethoate oxidation using a titanium dioxide mediated photocatalytic process [16]. By using the combination of a homogeneous system of UV/H_2O_2/Fe^{2+}, Badawy et al. [19] performed the elimination of many OPP pesticides. Whatever the AOP used, the treatment is not considered as complete and needs to be combined with biology to eliminate completely the organic matter [18].

Recently, many studies have investigated the persulfate ability to degrade organic pollutants [20 22]. Stable at ambient temperature, persulfate can be activated by metal reactions or by supplying energy (heat, UV, etc.). The energy supply resulting in cleavage of the peroxide bond of the persulfate molecule allows the formation of sulfate radicals (Eq. (1).

$$S_2O_8 + \text{Heat} \rightarrow 2SO_4^{\cdot-} \quad (1)$$

Heat activated persulfate degradation was studied on numerous organic compounds, such pharmaceuticals [23 25], endocrine disrupting chemicals [26 28], organochlorate herbicide [29 31], fongicides [32] and organophosphorus pesticides [33,34].

Electrochemical Advanced Oxidation Processes (EAOPs) are environmental friendly technologies which possess advantages over other technics: high efficiency, easy implementation and no chemicals addition is required [35,36]. Among EAOPs, one can cite electro Fenton oxidation H_2O_2/Fe_2 [35], photo electro Fenton oxidation H_2O_2/Fe^{2+} with UV/Vis (solar) radiation [37], and Electro Oxidation (EO) [38].

Because the oxidation of refractory compounds occurs at very high over potential, the choice of the anode material represents the key point. It is well known that electrochemical oxidation using a Boron Doped Diamond (BDD) anode represents a promising technique for the elimination of persistent organics [38 42]. Indeed, the strong oxidation ability of the BDD is due to the electrogeneration of hydroxyl radical ($^{\cdot}OH$) from the water discharge (Eq. (2).

$$H_2O \rightarrow \cdot OH + H^+ + e^- \quad (2)$$

On BDD anode, the hydroxyl radicals are quasi free on the surface and can react massively close to the anode with organics. The complete mineralization of the solution can be reached.

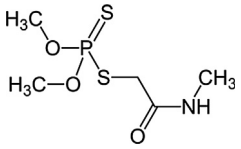
The aim of this work is to study and compare the oxidation of DIM by heat activated persulfate and by electrogenerated hydroxyl radicals in order to propose a process for the treatment of the unused pesticides solution before its discharge in the environment. The influence of the main operating parameters will be investigated. The complete disappearance of the target molecule will not be considered to be sufficient. Special attention will be paid on the variation of the biodegradability of the solution during both processes.

2. Materials and methods

2.1. Chemicals and solutions

The dimethoate (DIM) (≥98.5% purity) was purchased from Dr. Ehrenstorfer GmbH Company. All synthetic solutions were prepared with ultrapure water (ρ = 18.2 MΩ cm). The structure of DIM is reported in Table 1. Sodium peroxodisulfate (PS) (≥99% purity), Sodium sulfate (≥99% purity), were analytical grade and supplied by Merk and Sigma Aldrich. Other chemicals, organics or solvents were HPLC or analytical grade.

Table 1
Structure of the target molecule.

	Dimethoate (DIM)
Formula	$C_5H_{12}NO_3PS_2$
Molecular weight (g mol ^{1})	229.26
Structure	

2.1.1. Wastewater source

Danadim Progress, the commercial solution used by the farmers, was purchased from Cheminova and contains: DIM 400 g L^{-1}, cyclohexanone (43% weight), xylene (13% weight) and emulsifier (5% weight). The DIM concentration used in this study was set to 0.1 mM which corresponds to the DIM concentration used by the farmers for the phytosanitary treatments.

2.2. Analytical techniques

DIM concentration was measured by high performance liquid chromatography connected with an ultraviolet visible spectrometry detector (HPLC UV). The analyses were conducted on Agilent 1200 Series HPLC systems (Agilent Technologies, USA). A VYDAC C18 reverse phase 250 × 4.6 mm × 5 µm from Fisher Scientific was used. The detection UV wavelength was set to 200 nm. The mobile phase of HPLC is the mixture of ultrapure water/methanol (≥99.8% purity) with a ratio: 1/1 and the column temperature was set to 30 °C. The flow rate was 0.5 mL min^{-1} and the volume of injection was 10 µL. The detection limit of DIM is 0.3 mg L^{-1} and the quantification limit is 1.1 mg L^{-1} in Na_2SO_4 solution. The analytical errors range is 5.6% for 2 ppm in Na_2SO_4 solution. The total organic carbon, TOC, and inorganic carbon, IC, were measured with a TOC VCSN instrument (Shimadzu). The concentration of IC was measured after acidification and degassing, performed automatically. TOC was calculated from the difference between the total carbon and inorganic carbon. The chemical oxygen demand, COD, was determined by photometry using disposable test tubes (HI93754H 25 LR from HANNA Instruments) and a HACH DR/2400 photometer. Test tubes were heated at 160 °C for 2 h and left to cool down at room temperature before measurement. The analytic errors for TOC and COD were estimated to 5%.

BOD_5 was measured by a manometric respirometric method [43], using the OxiTop® Control system (WTW Weilheim, Germany). Nutrient solution was prepared using KH_2PO_4, K_2HPO_4, ($NaHPO_4{\cdot}2H_2O$), NH_4Cl, $CaCl_2$, ($MgSO_4{\cdot}7H_2O$) and ($FeCl_3{\cdot}6H_2O$). PolySeed™ capsules (InterLab®, USA) are used for seeding solution. In respirometric measurements, the measurement range of 0 80 mg L^{-1} was chosen and the samples volume was 365 mL. The bottles were sealed with a rubber sleeve containing a CO_2 absorber, sodium hydroxide pellet, immediately after the bottles were filled with the sample and the nitrification inhibitor *n* allylthiourea was added.

The measuring heads were screwed onto the bottles and the samples were stabilized in the incubation cabinet (20.0 ± 0.2 °C) for two hours before beginning the measurements.

After five days of incubation , BOD_5 was calculated by Eq. (3) :

$$BOD_5 = BOD_{st} \times DF \quad (3)$$

with BOD_{st}: the value read on the Oxitop and DF: Dillution Factor.

The concentration of Adsorbable organic halogens (AOX) contained in the electrolyzed solution was analyzed according to the ISO 9562 method [44] (by the Laboratoire Départemental 31: Eau Vétérinaire Air in Toulouse, France). The concentration of organohalogen compounds adsorbed on activated carbon is measured; this method is

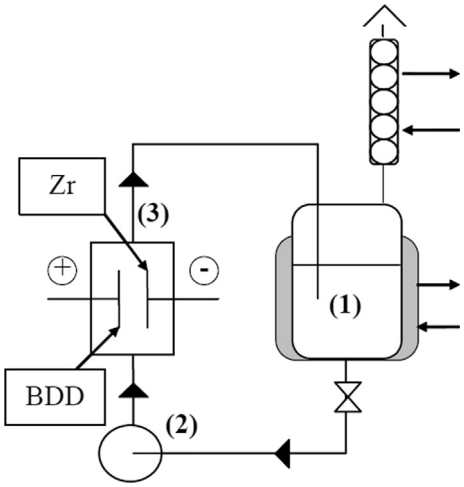


Fig. 1. Discontinuous process with a single compartment electrochemical reactor, (1) tank, (2) pump, (3) electrochemical cell.

applicable to concentrations of inorganic chloride ions less than 1 g L^{-1}. Samples with higher concentrations were diluted prior to the analysis.

2.3. Experimental set up

For the study using heat activated persulfate, the chemical reactor was a 1 liter thermoregulated batch reactor. The reactants Danadim and PS were stored in the stirred chemical reactor, the temperature was set at 60 °C.

For electrochemical oxidation, the solution was stored in a 1 liter thermoregulated glass reservoir and circulated through the cell using a centrifugal pump (Fig. 1). The flow rate was 360 L h^{-1} and the temperature was set at 30 °C. The electrochemical cell was a one compartment flow filter press reactor under galvanostatic conditions. Electrodes were two discs of 69 cm^2 of active surface. The BDD anode from Adamant (Switzerland) was elaborated by chemical vapor deposition on a conductive substrate of silicium. The cathode was a 1 mm thick disc of zirconium. The current was supplied by an ELCAL 924 power supply. Before each electrolysis, the working electrodes were anodically pretreated (40 mA cm^{-2} for 30 min in 0.1 M H_2SO_4) to clean their surfaces of any possible adsorbed impurities. Then, the system was rinsed by ultrapure water. Samples were taken at regular intervals in the tank. The global volume of samples was less than 10% of the total volume.

For an electrochemical reactor working in galvanostatic conditions, the energy consumption is given by Eq. (4):

$$E = I \times t/V \quad (4)$$

where I is the applied current intensity (A), t the electrolysis time (h) and V the volume of the treated solution (L).

3. Results and discussion

3.1. Oxidation by heat activated persulfate

As shown in Fig. 2, the degradation rate depends on the temperature. The degradation of DIM at 40, 50, 60 and 70 °C was fitted with a pseudo first order kinetics model. One obtains the constant rates of 0.0022, 0.0117, 0.0622, and 0.2394 min^{-1}, respectively. As seen from the inset panel of Fig. 2, the degradation of DIM correlates well with the Arrhenius behavior, resulting in a good linear relation with a function that can be written as Eq. (5):

$$\ln(k) = \ln A - E_a/RT \quad (5)$$

where A is the Arrhenius constant, E_a is the apparent activation energy (kJ mol^{-1}), R is the universal gas constant (8.314 × 10^{-3} kJ mol^{-1} K^{-1}), and T is the absolute temperature (K). This correlation allows to determine the apparent activation energy which is 140.6 kJ mol^{-1} close to the ones obtained for the degradation of p Nitrophenol (137.29 ± 0.03 kJ mol^{-1}) by thermally activated persulfate [45].

At 60 °C the quasi disappearance of DIM was reached within an hour. This temperature appears to be a good compromise in term of performance and energy consumption and has been chosen for this study. To ensure the stability of the solution at 60 °C, the measurement of DIM concentration has been carried out during two hours. No significant variation was observed. Fig. 3 shows the temporal variation of DIM concentration using various ratio of [DIM]°/[PS]° at 60 °C.

The complete degradation of DIM has been reached within 20 min, 35 min and 90 min for the 1/200, 1/100 and 1/50 of [DIM]°/[PS]°, respectively. Only 62% of DIM has been removed after 120 min in the case of 1/10 of [DIM]°/[PS]°. As shown in the inset panel of Fig. 3, the disappearance of DIM was found to fit well with a pseudo first order kinetics model, according to Eq. (6).

$$-\frac{d[DIM]}{dt} = k[DIM] \quad (6)$$

where k is the pseudo first order rate constant (min^{-1}), [DIM] is the concentration of DIM (mM). As shown in Fig. 4, the constant rate, k, varies linearly with the ratio [PS]°/[DIM]°. These results highlight that the concentration of PS has to be controlled in this process.

The influence of the PS concentration has been studied on the performance of DIM mineralization. Fig. 5 illustrates the variation of TOC, COD and DIM concentration during the reaction of DIM and PS using three ratio of [DIM/[PS]. It has been shown that the removal of TOC reached only 10% for the three ratios of concentrations. The same applies to the COD removal which reached only 5% for 1/10, 15% for 1/50 and 1/100 after 120 min of degradation.

We investigated the competition between other chemicals contained in the commercial Danadim (such as cyclohexanone, xylene and emulsifier) and DIM on the chemical reaction of sulfate radicals. The results obtained using Danadim are compared with the ones obtained using a synthetic solution containing DIM for [DIM]°/[PS]° = 1/50. Cyclohexanone, xylene and emulsifier present in Danadim represent 74% and 75% of the total COD and TOC, respectively. Fig. 5b evidences clearly that the degradation speed of DIM, COT and COD in both solutions is quite similar, showing that the presence of others compounds in the solution has no significant impact on the performances of the process.

In the light of the obtained results, one might wonder if the only disappearance of DIM is sufficient to render the wastewater biodegradable. Therefore the measurement of BOD_5 was performed during the chemical reaction of DIM with heat activated persulfate using a ratio of [DIM]°/[PS]° of 1/50 at 60 °C.

Fig. 6 shows that the COD decreases and becomes stable after just 15 min corresponding to 38% of DIM disappearance. The BOD_5 declines slowly before either stabilizing within 1 h. The BOD_5/COD ratio represents the biodegradability of the solution: a value more than 0.4 evidences that the solution is biodegradable [46].

The plot of BOD_5/COD shows that during the reaction of DIM with sulfate radicals, the solution becomes more toxic. This last result rules out the feasibility of treating a DIM solution by heat activated persulfate.

3.2. Electrochemical oxidation via hydroxyl radicals

Another way to oxidize the target molecule is the reaction with hydroxyl radicals. Because these radicals are very reactive (their half life is 10^{-9} s), they have to be generated in situ such as during the water oxidation using a BDD anode. A previous study has shown that

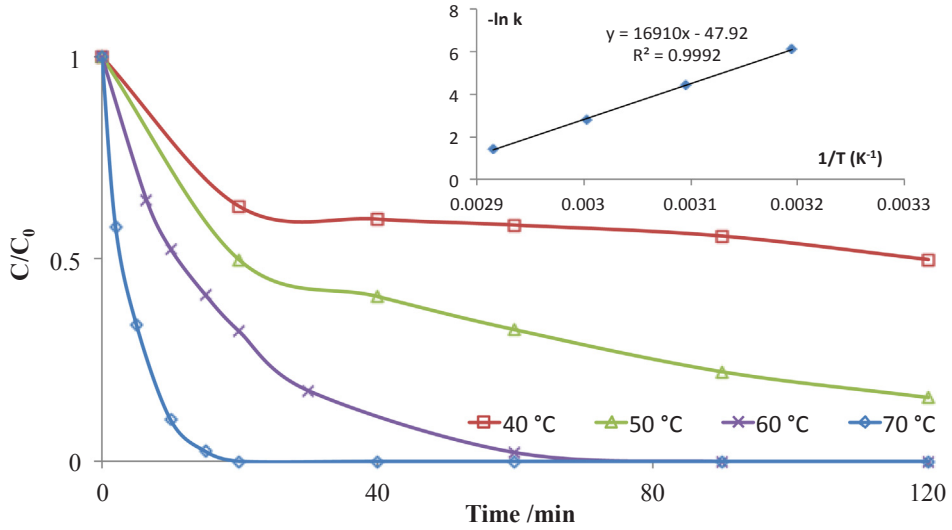


Fig. 2. Temporal variation of DIM concentration during heat-activated persulfate degradation. Inset panel: plot of –lnk vs time for various temperatures in the range of [40–70 °C]. Operating conditions: $[DIM]^0$ = 0.1 mM, $[PS]^0$ = 5 mM , V = 1L, Flow rate = 366 L h^{-1}.

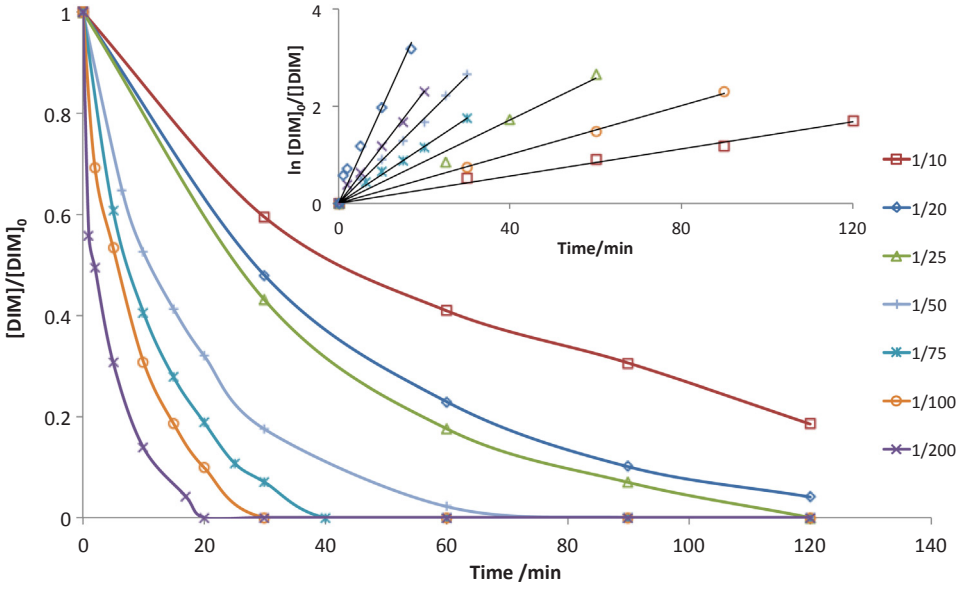


Fig. 3. Temporal variation of DIM concentration during heat-activated persulfate degradation. Inset panel: Pseudo-first order plot of DIM removal for various ratio of concentrations [DIM]°/[PS]° in the range of [1/200–1/10]. Operating conditions: $[DIM]^0$ = 0.1 mM, T = 60 °C, V = 1L, Flow rate = 366 L h^{-1}.

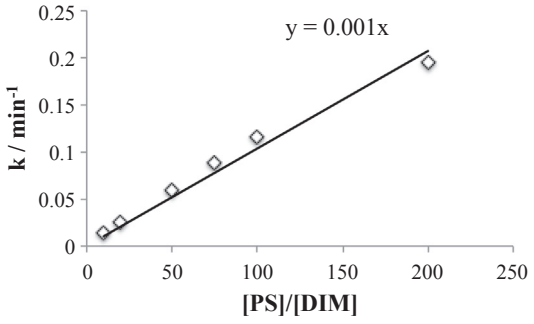


Fig. 4. Variation of the kinetic constant during the treatment of Danadim solution by heat-activated persulfate at various ratio of concentrations [PS]°/[DIM]° in the range of [10–200]. Operating conditions: [DIM]° = 0.1 mM, T = 60 °C, V = 1 L, Flow rate = 366 L h^{-1}.

the complete mineralization of DIM is possible using a BDD anode [38]. The influence of the applied current intensity and the type of used electrolyte were studied.

Fig. 7 shows the variation of DIM concentration during the elec trolysis of a 0.1 M Na_2SO_4 solution containing 0.1 mM of DIM using a BDD anode at 30 °C. The inset panel highlights that the DIM degrada tion follows a pseudo first order reaction (k = 0.0216 min^{-1}). The quasi complete disappearance of DIM (94%) has been reached after 120 min of electrolysis which requires an electrical consumption of 0.18 A h L^{-1} (using Eq. (4). Whereas 1 A h L^{-1} is necessary for a complete mineralization (94% of COD removal) [38].

By using a PbO_2 anode, Gargouri et al. showed that for a solution containing DIM (COD_0 = 320 mg L^{-1}), an energy consumption of 0.6 A h L^{-1} was required to remove 90% under optimized conditions [47].

From both economic and environmental perspectives, it is necessary to optimize the electrical consumption. The idea is to make the polluted solution biodegradable.

Fig. 8 shows the variation of COD, BOD_5 and BOD_5/COD ratio of

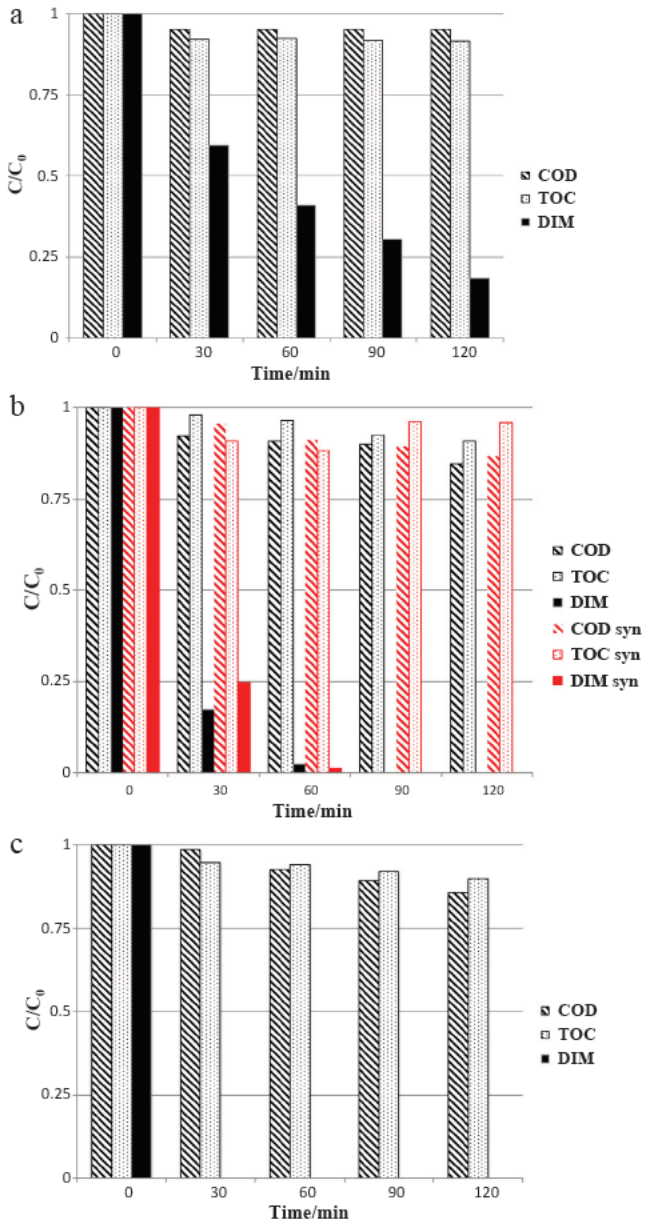


Fig. 5. Variation of COD, TOC and DIM concentration by heat-activated persulfate during the treatment of Danadim solution (in black and white) or synthetic solution containing only dimethoate (in red) at various ratios of concentrations [DIM]°/[PS]°: (a): 1/10, (b): 1/50 and (c): 1/100. Operating conditions: [DIM]° = 0.1 mM, T = 60 °C, V = 1 L, Flow rate = 366 L h^{-1}.

Danadim during the electrolysis containing 0.1 M Na_2SO_4. One can observe that BOD_5 sharply drops during the first hour of electrolysis and reaches 10 mg O_2 L^{-1} after 6 h. The BOD_5/COD ratio increases continuously during the electrolysis. The solution becomes easily biodegradable (> 0.6) after only 50 min (corresponding to an energy consumption of 0.074 Ah L^{-1}).

The presence of various salts in real wastewater and their impact in the process must be studied. Indeed, our previous study [38] also showed that the rate of DIM removal has been accelerated using chlorides as electrolyte because the reaction of these anions with hydroxyl radicals generates active chlorine species. However, due to the uncommon electrochemical properties of the BDD anode, the formation of perchlorate and halogenated organic compounds is possible. An electrolysis of Danadim containing 0.1 M of KCl was performed. The results presented in Fig. 8b show that the COD removal was low (40%)

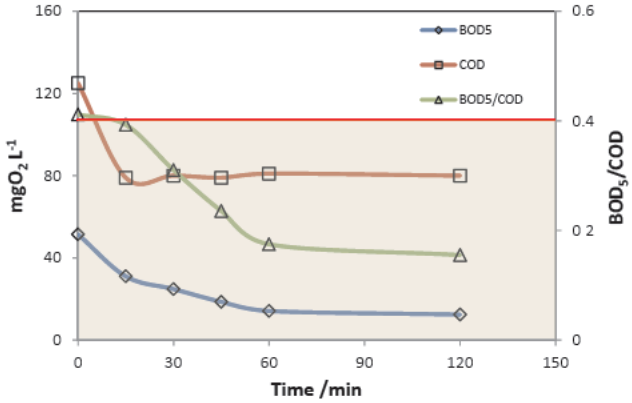


Fig. 6. Comparison of COD, BOD_5 and the biodegradability ratio during Danadim solution degradation by heat-activated persulfate for a [DIM]°/[PS]° ratio of 1/50. Operating conditions: $[DIM]_0$ = 0.1 mM, T = 60° C, V = 1L, Flow rate = 366 L h^{-1}.

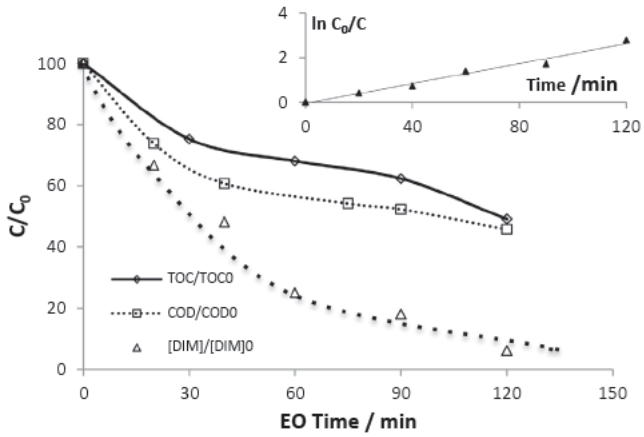


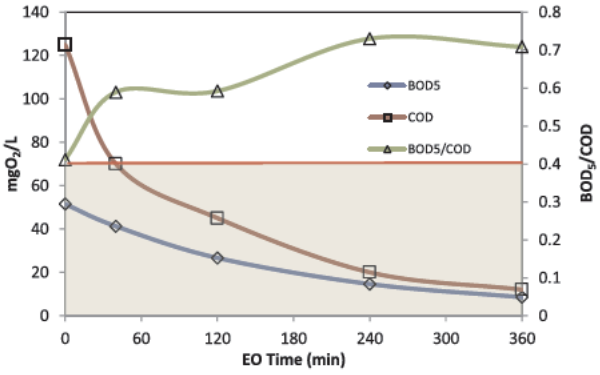
Fig. 7. Variation of TOC, COD and [DIM] during electrolysis of Danadim solution (1L). Inset panel: pseudo-first order plot for DIM degradation. Operating conditions: $[DIM]_0$ = 0.1 mM, $[Na_2SO_4]$ = 0.1 M, T = 30 °C, V = 1 L, i = 1.28 mA cm^{-2}, Flow rate = 366 L h^{-1}.

and stable after 2 h. The BOD_5 decreased to 5 mg O_2 L^{-1} after 1 h and then rose to 20 mg O_2 L^{-1} after 4 h. Consequently, the BOD_5/COD ratio decreased from 0.37 to 0.04 during the first hour of electrolysis and four hours were needed to reduce the toxicity of the solution and to render it biodegradable.

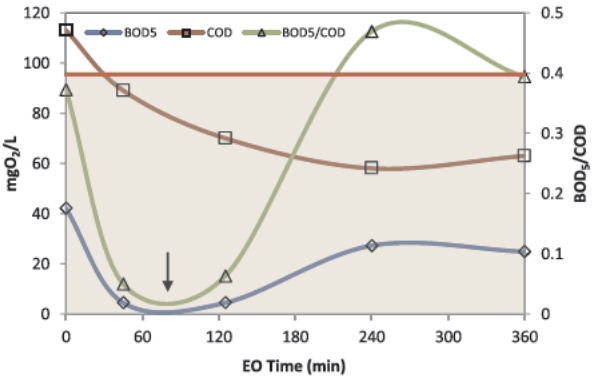
With the aim to explain the sharp increase of the toxicity of the solution during the first hour of electrolysis, the adsorbable organic halogen has been measured (Table 2). The AOX analyses confirm that the undesired halogenated organic compounds were generated continuously during the electrolysis which enhanced the toxicity of the solution. The comparison of Fig. 8a and b shows that although the rate of disappearance of the target molecule was accelerated in presence of chloride, the toxicity of the solution became more important during the process. To reach the biodegradability of the solution the required energy consumption corresponding to 4 h of electrolysis with a value of 0.353 A h L^{-1} was 4.8 times higher using chloride instead of sulfate as electrolyte.

4. Conclusion

The heat activated persulfate oxidation of dimethoate (DIM), an organophosphorus pesticide has been studied at T = 60 °C. The disappearance of the pesticide was quasi complete after 90 min using a [DIM]°/[PS]° ratio of 1/50 for a 0.1 mM concentration of DIM whereas



(a)



(b)

Fig. 8. Comparison of COD, BOD_5 and the biodegradability ratio during electrolysis of Danadim solution (1L) (a) $[Na_2SO_4]$ = 0.1 M (b) [KCl] = 0.1 M. Operating conditions: $[DIM]_0$ = 0.1 mM, , T = 30 °C, V = 1 L, i = 1.28 mA cm^{-2}, Flow rate = 366 L h^{-1}.

Table 2
AOX values during EO treatment of [DIM] = 0.1 mM in [KCl] = 0.1 M.

EO time/h	0	1	4
AOX/μg Cl L^{-1}	43	3360	6430

only 15% was mineralized, thus confirming the selectivity of sulfate radicals with organics. The simultaneous measurement of BOD_5 and COD has shown that the toxicity of the solution has enhanced during the reaction. This last point highlights that the use of the process for the treatment of water containing DIM must be avoided. Besides, the electrochemical oxidation of DIM using a boron doped diamond anode, showed that the disappearance of the target molecule is quasi complete after 120 min of electrolysis whereas only 50% is mineralized. The measurement of BOD_5 showed that only 50 min were required to render the solution biodegradable. However the presence of chloride ions in the process is not viable due to the generation of intermediates which are more toxic than the target molecule.

Acknowledgment

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